Spatial Variability of Pesticide Adsorption Parameters

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■ A comprehensive study comparing measurements of napropamide pesticide adsorption from two different methods, batch equilibrium and column flow-through methods, is reported. Thirty-six undisturbed soil columns were removed from a 0.6-ha field for the laboratory flow study, while 36 soil samples were taken from the sides of the holes formed by the columns for batch equilibrium adsorption measurements. Column measurements of the adsorption distribution coefficient, K_D, were inferred from breakthrough curves of chloride and napropamide. The field mean estimates of K_D from the batch and column measurements were similar ($2.01 \pm 31\%$ and $1.91 \pm 26\%$ (mL/g), respectively), but individual measurements were uncorrelated. Furthermore, no correlations were found between either K_D measurements and soil organic carbon fraction measurements. The distribution of organic carbon partiton coefficient, K_{oc}, values was more variable than the original K_D values.

Introduction

The last decade has been characterized by a growing concern over the pollution potential of pesticide chemicals applied to soil. The large number of pesticide chemicals in use, as well as the increasing number of new chemicals introduced each year, makes it impractical to perform a large number of comprehensive tests on each chemical to determine its mobility in a variety of soils. As an alternative, mathematical simulation models have been proposed to predict pesticide behavior in soils. The simplest models, combining equilibrium solid-phase adsorption with solution transport using either chromatography or convection–dispersion assumptions, have been successful in describing pesticide transport through laboratory soil columns conducted at low water application rates (*1–8*). As a practical measure, various simplifying assumptions are used in these models to reduce the number of parameters required in the equilibrium sorption characterization. The most common representation is a single-value linear relationship between the adsorbed concentration, S (μg/g), and the dissolved solution concentration, C (μg/mL),

$$S = K_D C \qquad (1)$$

where K_D (mL/g) is called the distribution coefficient (*9*).

For nonpolar organic pesticides, soil organic carbon content has been found to be the primary factor affecting adsorption (*10, 11*). This dependence has led to the development of an organic carbon distribution coefficient, K_{oc}, which is defined as

$$K_{oc} = K_D/f_{oc} \qquad (2)$$

where f_{oc} is the soil organic carbon fraction. This param-

eter has been shown to have a smaller coefficient of variation between different soils for a given pesticide than the distribution coefficient, K_D, (10). Even more standardized indexes for adsorption have been proposed. Comparison of values from a number of different studies has demonstrated a significant linear correlation between the logarithm of K_{oc} and the logarithm of the octanol–water partition coefficient, K_{ow} (11, 12). Furthermore, some success has been achieved in estimating K_{ow} from chemical structure (11–14). These simple adsorption indexes together with transport models thus allow one to estimate relative pesticide mobility over a wide range of soils and conditions with few measurements. However, the correlation between K_D and organic matter is less significant in soils low in organic matter, where competition with mineral adsorption sites becomes more important (15).

Furthermore, use of the distribution coefficient to represent transport through natural soils suffers from several serious limitations. The first limitation arises from the nature of the measurement technique, batch equilibrium, which measures the maximum possible adsorption in a soil that has been completely dispersed (6, 16). For this reason, soil column displacement estimates of adsorption have been suggested as an alternative method to the batch equilibrium procedure in order to provide more realistic values for K_D (16–17).

The second significant limitation of the K_D concept for natural soils is caused by the spatial variability of soil properties over large field areas. Although K_D measurements coupled with transport models have been successful in describing laboratory phenomena, the laboratory K_D measurement did not provide an accurate prediction of observed field behavior in several studies (18, 19). Although the field experimental evidence is rather limited, even for mobile chemicals that act as water tracers, recent experiments suggest that laboratory scale models may not accurately describe transport under field conditions where extensive lateral and vertical variability cause local variations in transport that are difficult to represent from a single average coefficient (20–23).

Although the distribution coefficient, K_D, or similar single indexes for adsorption may not be adequate to quantitatively characterize transport under field conditions, they may still be useful as indexes of relative mobility to classify pesticides into different categories (24). Before this may be established, however, research is needed on extent of variability of K_D or its equivalent under natural conditions and also on the degree to which laboratory scale correlations are still valid on the field scale. The research reported in this paper addresses several of these needs by first observing the spatial variability of the distribution coefficient across a large field as measured by both the flow-through and batch equilibrium procedures and finally by testing the organic carbon–K_D correlation on a large number of replicates obtained in the field.

Materials and Methods

The samples used in this study were obtained from the inner 0.64 ha of an experimental field containing bare Tujunga loamy sand (mixed, thermic, Typic Xeropsamments) located in Etiwanda, CA. This field had been under continuous cropping for the 5 years previous to the experiment, but was cleared and leveled 1 month prior to sampling. The field was divided into 36 sampling locations on a 6 × 6 square grid, and three sets of samples were taken at each site. First, a set of 36 "undisturbed" soil cores were taken by slowly inserting 10 cm diameter columns into the soil to a depth of 15 cm and removing the intact cores. These columns were used for bulk density

and water content measurements and for the flow experiments. Second, a set of 36 bulk soil samples were taken by compositing soil taken from the top, middle, and bottom of the wall formed from the undisturbed soil columns. These samples were used for the batch adsorption isotherm studies. Third, a set of 36 soil cores were taken to a depth of 120 cm at locations within 1 m of the earlier measurements using a hydraulic auger. Each core was divided into 10-cm increments, bagged, and kept refrigerated prior to organic carbon content analysis.

Column Study. The 36 undisturbed soil columns were taken to the laboratory and were used for chemical leaching experiments under a steady-state water flux rate of 4 cm/day, in groups of eight columns at a time. Each of the 36 columns was irrigated by using a 30-cm-long 24-gauge hypodermic stainless-steel tube (0.03 cm i.d.). A constant head of 40 cm was maintained over the tubes, producing a flow rate of approximately 4 cm/day over each column. The irrigation solution consisted of 8 mequiv/L $CaSO_4$ solution treated with a small concentration of $CuSO_4$ to prevent algal growth. The top of each column was covered with a plastic cap to prevent evaporation. Each cap had a pin hole through which the hypodermic needle was inserted to drip at the center of the column. The entire soil surface remained moist during the experiments. A copper screen was attached to the bottom of each column to contain the soil. The drainage solution was collected in 0.5-L narrow-neck columns by placing the columns on top of funnels and placing the bottles under the funnels.

After steady-state water flow was reached, a 0.5-cm pulse of 8 mequiv/L $CaSO_4$ and 50 mg/L napropamide (2-naphthoxy)-N,N-diethylpropionamide) was applied. The drainage water was sampled at 4-h intervals and was analyzed for chloride and napropamide concentrations. The chloride concentration was measured in the effluent collected from the bottle with an Aminco analytical chloride titrator. The napropamide concentrations were measured after extraction by hexane (1:9 water:hexane) using a Varian gas chromatograph.

Batch Adsorption Determination. The adsorption isotherms were determined by using 10-g soil subsamples, which were mixed with 10 mL of napropamide solution and placed in 50-mL centrifuge tubes made of Teflon. The tubes were first capped with rubber screw-in stoppers lined with thin sheets made of Teflon and then were mounted on a wrist-action shaker in a constant temperature (20 °C) incubator for 24 h. Subsequently, the samples were placed in a refrigerated centrifuge (20 °C) at 15 000 rpm for 20 min. a 1-mL sample of the supernatant solution was mixed with 20 mL of scintillation solution (25) in a 25-mL glass vial. The sample vials were kept and placed in the scintillation counter. A refrigerated Beckman liquid scintillation system was used in the analysis. Each sample was counted three times for 3 min or until the counting error was less than 1%. Initial pesticide concentrations used in the batch experiment were 1, 3, 7, 20, and 45 mg/L napropamide in 0.01 N $CaCl_2$ solution. Three milliliters of radioactive napropamide (4.4 mg/L) was added to 500 mL of initial solution, resulting in an increase of 0.0264 mg/L in the concentration of napropamide initial solutions.

Organic Carbon Determination. The Walkley–Black procedure (26) was used in determining organic carbon content.

Theory

The distribution coefficient was estimated from the soil column transport experiments by the following procedure.

The chloride and napropamide effluent concentrations were collected as a function of time or equivalently of cumulative column drainage, I (cm), and the corresponding curves were normalized so that the area under the curves was unity. This normalization was achieved by dividing each concentration by the quantity

$$M = \int_0^\infty C(t') \, dt' \approx \sum_{J=1}^{N-1} \bar{C}(t)(t_{J+1} - t_J) \qquad (3)$$

where M is the cumulative solute mass/area leached from the column, N is the number of data points, and $\bar{C}(t_J) = (C(t_{J+1}) + C(t_J))/2$.

The new normalized concentrations were used to estimate effective solute velocities by the method of moments (27). In this procedure, the experimental first concentration moment is equated with the theoretical value of the first moment, where the moment is calculated by

$$T_1 = \int_0^\infty C(t)t' \, dt' \approx \sum_{J=1}^{N-1} \bar{C}(t_J)\bar{t}_J(t_{J+1} - t_J) \qquad (4)$$

where $\bar{t}_J = (t_{J+1} + t_J)/2$. The value of the theoretical concentration moment depends on the model used in the moment integral. For both the two-parameter convection dispersion equation (2) and the four-parameter mobile–immobile water convection dispersion equation (3), the theoretical value of the first concentration moment is given by

$$T_1 = L/V \qquad (5)$$

where L is the location where the concentration is measured and V is the effective velocity of the solute. This velocity is in turn related to the pore water velocity, V_P, of a mobile noninteracting solute by

$$V = V_P/R \qquad (6)$$

where the partition coefficient, R, is given by

$$R = (1 + \rho_b K_D)/\theta \qquad (7)$$

where ρ_b (g/cm^3) is dry soil bulk density and θ is the volumetric water content. Each of these models assumes that adsorption is linear, reversible, and proceeds to equilibrium.

In our experiments we assumed that chloride was a perfect water tracer and therefore that the chloride velocity was equal to the pore water velocity ($V_{CL} = V_P$). Thus, the partition coefficient, R, of the napropamide was given by

$$R = V_{CL}/V_{NA} \qquad (8)$$

where the velocities were calculated by using the measured concentration moments and eq 5, and the distribution coefficient was calculated by using eq 7 and measured values of ρ_b and θ.

Results

Batch Equilibrium Studies. The batch adsorption data for each of the 36 sites were fitted both to the linear model, eq 1, and also to a nonlinear Freundlich model

$$S = K_F C^{1/N} \qquad (9)$$

where K_F is the Freundlich coefficient and N is a constant. Figure 1 shows a plot of all curves plotted simultaneously. Although there are significant differences between different sites, each individual record is quite linear. In 32 of the sites there was no significant difference ($P = 0.01$) between the Freundlich and linear fits to the model. Therefore, the linear model, eq 1, was used in all cases. The average K_D for all sites with the batch equilibrium
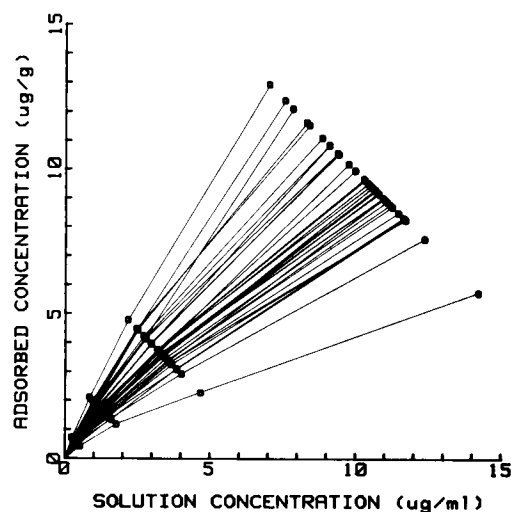

Figure 1. Batch equilibrium adsorption isotherm for each of the 36 soil samples used in the batch study.
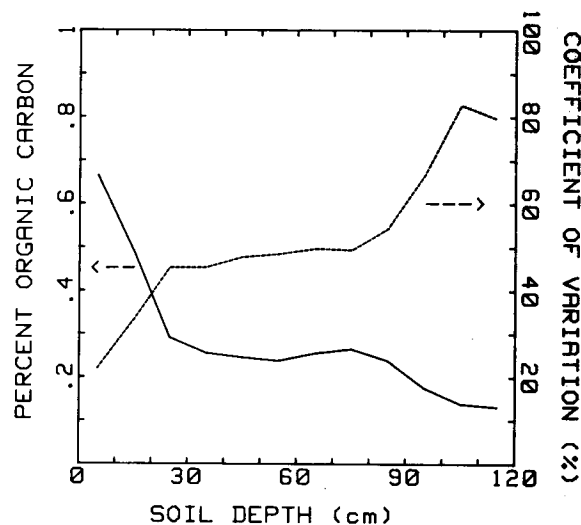

Figure 2. Percent organic carbon vs. soil depth averaged over all 36 replicates at each of the 12 depths in the study. Also shown is the sample coefficient of variation at each depth.

data was 2.01 mL/g with a coefficient of variation of 31%. The distribution of K_D values was approximately normal.

Organic Carbon. Figure 2 shows the field average organic carbon fraction as a function of depth for the 36 sites along with the coefficient of variation for each depth. The surface 30 cm is significantly higher in organic carbon than the lower depths, although the coefficient of variation of the lower depths rises to a higher level than the surface. The small mean values less than 1% are typical of sandy soils in arid regions.

Soil Column Experiments. Figure 3 shows a typical pesticide drainage concentration record (solid line) for three of the columns, together with the convection–dispersion equation representation of the concentrations (dotted lines) using pesticide model parameters estimated by the method of moments. Also shown in Figure 3 is the prediction of the convection–dispersion equation (dashed line) using the distribution coefficient measured in the batch study on the soil sample taken from the same site as the column. This K_D value was used to calculate a partition coefficient, using eq 7, that was combined with the measured chloride velocity to estimate the pesticide velocity, using eq 6. The same dispersion coefficient was used to both the dashed and dotted curve simulations. These three columns represented cases where the batch
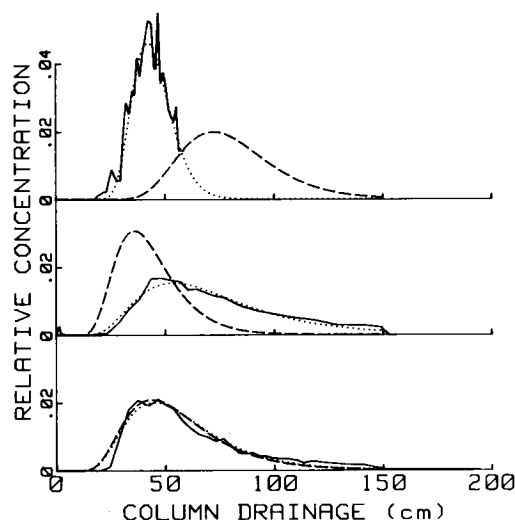
Figure 3. Napropamide concentration vs. cumulative drainage (solid lines) for three of the soil columns. Also shown are simulations of the convection dispersion equation using parameters fitted by the method of moments (dotted lines) and using batch equilibrium estimates of K_D (dashed lines).

Table I. Mean, Standard Deviation (SD), and Coefficient of Variation (CV) of Different Adsorption Parameters Measured in the Field Study

parameter	mean	SD	CV	N
K_D batch, mL/g	2.01	0.63	31	36
K_D column, mL/g	1.91	0.49	26	36
K_{oc} batch, mL/g	363	137	38	36
K_{oc} column, mL/g	333	85	25	36
f_{oc}, 0–10 cm	0.007	0.001	22	35
f_{oc}, 10–20 cm	0.005	0.002	33	34
ρ_b, (g/cm^3)	1.38	0.08	6	36
θ	0.29	0.01	5	36
% clay, 0–30 cm	4.6	0.005	1	13

K_D value was larger than (top figure), smaller than (middle), and similar to (bottom) the K_D value measured in the column method.

Discussion

Table I summarizes the field mean values, standard deviations, and coefficients of variation for all parameters measured in the field experiment. All samples were found to be statistically independent of each other by constructing a semivariogram (28). Included also for reference are values of percent clay obtained from an earlier study on the site. The batch equilibrium and column K_{oc} values were obtained from the organic carbon values at each site averaged over the 0–20-cm layer using eq 2.

Several significant conclusions may be drawn from this table. First, the similar mean values between the batch and the column K_D values offer evidence that, on average, adsorption was proceeding to equilibrium at the flow rates used in the column experiments. If adsorption had been strongly rate limited in the column experiments, the average K_D determined by this method would have been considerably smaller than the average batch K_D. Second, use of an organic carbon distribution coefficient increases rather than decreases the coefficient of variation of the samples, indicating that variability among replicates may not be solely attributed to variations in organic carbon content. It seems likely that in our sandy soil the adsorption site composition is quite heterogeneous.

A major goal of this research study was to determine the extent to which the batch equilibrium and flow-through methods represent equivalent indexes for adsorption of
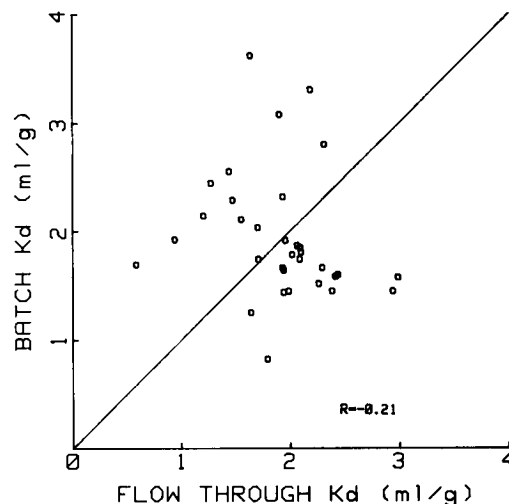

Figure 4. Scatter diagram between K_D measured by batch equilibrium and column flow methods ($N = 36$).

Table II. Correlation Coefficients between Adsorption Parameters Measured in the Field Study ($N = 36$)

X	Y	$r(XY)$
K_{D_B}	$K_{D_{col}}$	−0.21
K_{D_B}	f_{oc} (0–20)	−0.06
$K_{D_{col}}$	f_{oc} (0–20)	0.57
$K_{D_{col}}$	ρ_b	−0.32

organic chemicals, particularly in cases where rate limitations are not present. Figure 4 presents a scatter diagram showing the correlation between the batch and column measurements of K_D at the 36 sites. The complete lack of correlation is surprising, given that both field average estimates are similar and that the soil used in each individual batch determination was obtained from the sides of the holes formed by the soil columns. Table II extends the correlation analysis to other potentially relevant parameters in the adsorption process. As seen, the correlation between organic carbon fraction and distribution coefficient is not particularly high for either the batch or flow-through methods, which is consistent with the earlier findings that the organic partition coefficient did not decrease the coefficient of variation among the replicates.

Although the column outflow concentrations from the undisturbed soil columns showed considerable structure, most of them could be simulated quite well by the conversion dispersion equation when the parameters are fitted by the method of moments (Figure 3). Most surprising about the lack of agreement between batch and column measurements are for those cases (e.g., the middle of Figure 3) where the batch method predicted less adsorption than was observed in the columns. This occurred at 18 of the 36 sites.

A possible explanation for the lack of agreement in these experiments is adsorption hysteresis, which would retain solute in the columns and broaden the effluent curve. If this is a significant effect, it could be avoided by using continuous solute applications to the columns rather than pulses. However, it should be pointed out that the two-parameter model without hysteresis does describe the outflow shapes very well without using hysteresis when the parameters are optimized (Figure 3).

Concluding Remarks

The experimental findings summarized in this paper present a rather discouraging picture for the characterization of pesticide transport under natural field conditions.

Individual measurements of adsorption coefficient by either method varied by approximately 30% across a 0.64-ha field. Furthermore, indexes that should represent equivalent measures of adsorption under conditions where equilibrium is reached yielded estimates with little or no correlation to each other on samples that were spaced as near as possible to each other across the field. This lack of correlation should be taken as a warning that transport under natural conditions may be too complex to permit a simple index such as a distribution coefficient to be used for describing the adsorption process.

However, a 30% coefficient of variation across a 0.64-ha field does not represent an insurmountable level of variability. Use of an average value based on a limited number of replicates may actually characterize behavior adequately for use in model characterization of a new candidate chemical, consistent with the goals discussed at the beginning of this paper. However, it remains to be shown whether these indexes actually describe important characteristics of pesticide transport under natural conditions.

Registry No. Napropamide, 15299-99-7.

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